GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: April 8, 1971

Project Title: Research Initiation - Stress Crazing in Crystalline Polymers

Project No: B-519 (E-19-607)

Principal Investigator Dr. John D. Muzzy

Sponsor: National Science Foundation

Agreement Period: From April 1, 1971 Until September 30, 1972

Type Agreement: Grant No. GK-27851

Amount: $16,000 NSF Funds (B-519)
13,328 Ga. Tech Contribution (E-510)
$29,328 Total

Reports Required: Annual Letter Technical (short, informal) due March 31, 1972.
Final Letter Technical due upon completion (September 30, 1972.)

Sponsor Contact Person (s): National Science Foundation
Division of Engineering
Attention: Dr. R. J. Reynik - Engineering Materials Program
Washington, D.C. 20550

Assigned to: School of Chemical Engineering

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RA-3 (2-71)

GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT TERMINATION

August 1, 1973

Date: _____

Project Title: Stress Crazing in Crystalline Polymers - Research Initiation

Project No: E-19-607 (old B-519)

Principal Investigator: Dr. John D. Muzzy

Sponsor: National Science Foundation

Effective Termination Date: 3/31/73 (Final Report Due)

Clearance of Accounting Charges: by 3/31/73

Grant/Contract Close-out Instructions: Final Fiscal Report

School of Chemical Engineering

Assigned to: _____

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RA-4 (6-71)

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

March 28, 1972

Dr. R. J. Reynik
Engineering Materials Program
National Science Foundation
Washington, D. C. 20550

Dear Dr. Reynik:

Attached is an annual technical letter for the NSF research initiation grant number GK-27851 entitled: "Stress Crazing in Crystalline Polymers". The research has progressed to the stage where the proposed experiments can be performed. We are proceeding with these experiments and expect to have sufficient data for publication by March 31, 1973 -- the termination date of the grant.

If you have any questions concerning the work please contact me at (404) 894-2871. I would be pleased to have a member of your staff visit our laboratories and discuss our work.

Sincerely,

John D. Muzzy
Assistant Professor

JDM:np

ANNUAL TECHNICAL LETTER

Georgia Institute of Technology
Principal Investigator: John D. Muzzy

Grant No.: GK-2781
Starting Date: 4/1/71
Completion Date: 3/31/73
Grant Title: Stress Crazing in Crystalline Polymers
Research and Results:

The primary objective of this research is to study the mechanical degradation of crystalline polymers by the process of crazing under a tensile stress resulting in the formation of microvoids. Specifically, the craze morphology of samples crystallized under different conditions will be examined from the inception of crazing to the formation of an ultimate morphology. The problem is analogous to a kinetic study of consecutive reactions.

The purpose of this research is to understand the mechanism of mechanical failure by crazing in order to devise methods for preventing or controlling crazing in crystalline polymers. Prevention or control of crazing would increase the energy required for mechanical failure of crystalline polymers and would also permit greater control of fabrication processes in which orientation of solidified polymer occurs.

During the first year, the major research effort has been devoted to the design, fabrication and evaluation of the specialized equipment needed for this program. The major items constructed during this period are (1) a compression mold for forming the $\frac{1}{4}$" thick tensile samples which span 4" x 10"; (2) a thermal gradient crystallization (TGC) cell which is capable of isothermal crystallization or crystallization under a specified thermal gradient across the sample thickness at a controlled cooling rate; and (3) tensile

grips and fixtures for deforming the 4 inch wide samples within an environmental temperature chamber using an Instron Universal Testing Machine. All of these devices have been subjected to evaluation since their construction.

Considerable time has been devoted to determining suitable conditions for molding uniform samples of the high density polyethylene. A recurring problem has been the formation of internal voids due to crystallization. This difficulty has been minimized by forming the powder under high pressure just below the melting point. These samples have a uniformly dispersed void content which can be eliminated in the crystallization step. Since this technique may not provide adequate uniformity, a new forming device is under construction which will permit us to slowly extrude sheet through a slot die. We also attempted to obtain $\frac{1}{4}$" thick sheet of high density polyethylene commercially but could not find a supplier. This difficulty in forming or finding $\frac{1}{4}$" thick sheet has prevented us from generating the desired research information at this juncture, but this impasse has just been resolved.

The thermal gradient crystallization (TGC) cell has undergone preliminary evaluation and it appears to meet our objectives. The TGC cell is a sandwich type construction which, in cross section from the center of the sample, consists of 1/8" aluminum, a $\frac{1}{4}$" air duct and then insulation on each side. The sample is also surrounded by a Teflon blank on its periphery and the complete sandwich is clamped to provide good thermal contact. Each air duct is heated separately by hot air without recycle. High air velocities through the ducts are maintained to minimize the temperature drop along the flow path. With this design the temperatures in the air ducts can be independently controlled and temperature changes in the air ducts can be generated virtually instantaneously. The cooling rate is primarily limited by the thicknesses and thermal conductivities of the sample and aluminum barriers. With the current sheet thicknesses of $\frac{1}{4}$" for the polyethylene sample and 1/8" for the aluminum we have

generated a maximum constant centerline cooling rate of 12.5°C/minute. Specific constant cooling rates of less than 12.5°C/minute can be generated by a chain link drive on the powerstats supplying energy to the air heating elements. Presently the TGC cell is being calibrated.

The sample grips for the tensile deformation have been tested using low density polyethylene samples. The grips performed satisfactorily.

As indicated above the material selected for the initial study is high density polyethylene; in particular, Marlex 6050 powder manufactured by Phillips Petroleum Company. This choice is based on the considerable information which has been published on the characterization of this material. The choice is also based on the relative ease of working with polyethylene and the foreknowledge that the craze morphology of interest can be generated within this material. The study of other polymers is planned in ensuing research.

During this first year of the initiation grant a Porter Blum MT-2B ultramicrotome has been purchased and tested. This microtome will be used extensively once the morphological characterization of the samples can be carried out.

Also, during this first year an ongoing computer search of the literature on the subject of crazing and mechanical failure of polymers has been established and a differential scanning calorimeter has been set up and calibrated for use in sample characterization.

In summary, the work done to date has been devoted to setting up and evaluating the specialized equipment intended for this research program. We are now prepared to carry out the tests and characterizations originally planned for this research program.

Publications: Further work must be done before this research can be published.

Theses: This research will comprise the Ph.D. thesis of Roger D. Hester.

Scientific Collaborators: Roger D. Hester, a Ph.D. candidate in the School of Chemical Engineering, has worked on this research since the inception of the NSF grant and will continue working on this research until his thesis is completed.

Comments: An application for a continuation grant will be submitted once meaningful results are generated. Also, as an outgrowth of this initial research, related research programs are being developed. For example, with the use of the thermal gradient crystallization cell it is possible to crystallize samples in which crystalline growth is predominantly parallel to the sample thickness rather than random. In essence, a simplified morphology should result with a lamellar structure which can be more readily characterized. A second program under development is a method for characterizing inter-lamellar regions and crazes with minimal structural disruption by gas and liquid permeation studies in conjunction with existing characterization techniques.

3/28/72

E-14-607

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

June 22, 1973

Dr. R. J. Reynik
Engineering Materials Program
National Science Foundation
Washington, D. C. 20550

Dear Dr. Reynik:

Enclosed are two copies of the final technical letter for the NSF research initiation grant number GK-27851 and two copies of an ACS paper presented on this research. Please accept my apology for the delay in completing the final technical letter - I wanted to assemble the ACS paper and include as much of our recent results as possible.

Although the grant period has ended, our research is definitely continuing. Due to the NSF grant, I have been able to initiate a number of promising research programs. Unfortunately, I have not been able to obtain funds to support this research to the extent I would like; but I shall keep trying.

I thank you for your consideration and NSF for supporting this research.

Sincerely,

John D. Muzzy
Assistant Professor

JDM/wjp
Encl.

FINAL TECHNICAL LETTER

Georgia Institute of Technology

Principal Investigator:	Dr. John D. Muzzy
Grant Number:	GK-27851
Starting Date:	April 1, 1971
Completion Date:	March 31, 1973
Grant Title:	Stress Crazing in Crystalline Polymers

Research and Results

The primary objective of this research is to study the mechanical degradation of crystalline polymers by the process of crazing under a tensile stress resulting in the formation of microvoids and microfibers within the c rystalline polymers. A fundamental knowledge of the crazing process can be utilized to devise methods of preventing or controlling crazing. By either prevention or control of crazing the energy required to cause ductile failure can be increased. Also, controlled crazing can be utilized to form fibrillated yarns and semi-permeable membranes.

The goals, experimental approach, results and current conclusions of this research program were presented April 13, 1973 to the 165th National Meeting of the American Chemical Society. Two copies of this presentation are enclosed. The results and conclusions are summarized below:

1. Crazes form in crystalline polyethylene after less than 20% extension before necking begins.
2. Crazes form preferentially at morphological discontinuities, particularly spherulite centers and boundary regions.

3. The crazes are extended in the direction of deformation through the neck region.
4. The deformation of crazed regions exceeds the macroscopic deformation whereas the uncrazed portion of the spherulites experience relatively less deformation.
5. The density and heat of melting of deformed polyethylene does not change significantly up to a draw ratio of four indicating little change in crystalline structure.
6. Cryogenic sectioning followed by chromic acid etching is a useful technique for preparing polyethylene for observation by scanning electron microscopy.
7. Cryogenic sectioning of polyethylene reduces artifacts due to cut marks and surface smearing.
8. Chromic acid etching removes material from polyethylene surfaces rapidly without changing the density and mechanical integrity of the polyethylene.

Publications

This research has not been published to date since more work is required. Preliminary results were presented at the 165 th ACS National Meeting and two copies of this presentation are enclosed. The following paper based on this research has been accepted for publication:

Muzzy, J. D., Hester, R. D. and Hubbard, J. L., "Chromic Acid Etching of Polyethylene," Proceedings of the Electron Microscopy Society of America, New Orleans, La. (Aug. 1973) (in press)

Further publications are planned, particularly as Mr. Hester's thesis on this subject nears completion during the remainder of this year.

Thesis: This research will comprise the Ph.D. thesis of Roger D. Hester.

Scientific Collaborators: Roger D. Hester, a Ph.D. candidate in the School of Chemical Engineering, has worked on this research since the inception of the NSF grant and will continue working on this research until his thesis is completed.

Comments

A proposal was submitted to the NSF pertaining to this subject which has been rejected. A second proposal concerning the use of stress crazing to form fabric from films has been prepared for inclusion in a RANN proposal from the Textile School at Georgia Tech.

This research initiation grant has provided the principal investigator the time and means to launch a research program on the basic problem of stress crazing in crystallene polymers. This research will be continued. A number of related research programs have also been initiated as a consequence of this grant. These include:

1. Computer simulation of non-isothermal polymer crystallization.
2. Use of stress crazing as a method of fabricating membranes, fabrics and synthetic paper.
3. Chromic acid etching of polyethylene for morphological examination.
4. Structure and properties of thermal gradient crystallized polymers.
5. Effect of molecular parameters on polymer crystallization.

Recently, a second Ph.D. candidate, Mr. Donald Bright, has elected to do his thesis work in this area.

THE EFFECT OF CRYSTALLINE MORPHOLOGY ON STRESS CRAZING IN POLYETHYLENE

Roger D. Hester and John. D. Muzzy
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia

Presented at the 165th ACS National Meeting, Dallas, Texas, April 12, 1973

INTRODUCTION

The inception of plastic deformation in a polymer under a tensile stress often begins by some form of void formation. Due to the great molecular length of polymer molecules, material may traverse the void regions as fibrils as shown in Figure 1. Without the fibrils this type of void is called a crack whereas with fibrils this region is called a craze. Unlike a crack, a craze can support a stress. Commonly, the fibrillar/void structure of the crazes is of sufficient size to scatter light; hence, stress crazing can be visually observed as stress whitening.

Stress crazing is important because it is an early indication of mechanical failure and occurs in the commercially important processes of fiber and film drawing. The microfibrous structure and properties of drawn material is a result of the formation, growth and deformation of crazes in the yielding process.

The primary intent of this research program is to characterize the crazing process: i.e., where crazes form, how many form, what happens to them and how crazing can be controlled through modifications of the molecular and solid state structure of the material prior to deformation. For example, Thomas and Hagen (1) have shown that reducing the molecular weight distribution in polystyrene reduces the size but increases the

number of crazes occurring in yielding. Ultimately, the information generated can be utilized to improve the ductility of polymer products, to control the porosity of oriented films and to modify the microfibrous texture of drawn fibers.

EXPERIMENTAL APPROACH

We decided to use large bulk samples -- 0.22 inches thick -- in order to ascertain both the surface and internal response to deformation. Also the large samples enables the study of a particular state of deformation in one sample by a number of techniques.

We have used Marlex* 6050 because it has been well characterized. In future work, we intend to study modifications of this linear polymer -- particularly higher molecular weight versions and butene copolymers -- in order to assess the effect of molecular structure on crazing.

We have used a fixed rate of cooling to crystallize our bulk samples because this approximates commercial practice.

Drawing conditions are important variables in the crazing process as reported by Muzzy and Hansen (2). However, the drawing conditions were fixed at 60°C and 40% per minute extension -- Figure 2. These conditions produced uniform samples which exhibited stress whitening indicative of crazing -- Figure 3. As shown in Figure 4 the macroscopic draw ratio versus axial length is relatively uniform.

Since the structure of crazed material is complicated, we decided to characterize the craze morphology by starting at low magnifications. Consequently, we start with polarized light microscopy, then scanning electron microscopy and end at very high magnifications with the transmission

*Trademark, Phillips Petroleum Co.

electron microscopy. We intend to follow up with light and x-ray scattering techniques later.

Because we rely on microscopic examinations it is imperative that we minimize artifacts which can arise in preparing the samples for observation. The surface structure shown at the top of Figure 5 is not typical of the bulk material; hence, we decided to section the samples and examine the internal structure. However, sectioning can introduce cut marks and smear the material as shown in Figure 6. Cold sectioning improves the quality of the surface, Figure 7, but only faint structural features can be discerned. To accent polyethylene structural details, Peterlin has treated samples for one week at 80°C with fuming nitric acid (3). We tried a similar approach at 60°C, not wanting to exceed our drawing temperature. Our treated samples increased in density, lost mechanical strength and frequently burst apart. Desiring a better etch, we used a 6 molar solution of chromic acid at 60°C for varying time periods. With this treatment no change in density or mechanical integrity is evident and structural features are enhanced.

EXPERIMENTAL RESULTS

The size of our samples and the construction of our crystallization apparatus, Figure 8, controls our crystallization capabilities. The maximum centerline cooling rate we can get is 8°C/min. Thus, due to the kinetics of polyethylene crystallization, we cannot isothermally crystallize below 115°C. Alternatively, if we crystallize above 118°C, our samples will not draw. We are now starting some work on quenching thinner sheets to get more variation in initial morphology. Our present samples were cooled from the melt to room temperature at 8°C/min. Due to the large heat of fusion (69 cal/g.) the sample cooling rate probably is considerably less than 8°C/min.

for a short period of time once rapid crystallization begins.

The resulting samples exhibit significant structural variations parallel to their thickness. This morphological variation is most evident in looking at the ring spacing of the spherulites from the surface to the centerline -- a distance of approximately 2800 microns in Figure 9. Beyond a depth of 1500 microns, ringed spherulites are not evident. The density and heat of melting also increase moderately in value towards the centerline. These trends suggest that the material crystallized at progressively higher temperatures towards the centerline. Hence, our objective of achieving a range of crystalline morphologies is obtained in one sample.

In discussing the early stages of drawing using a polarized light microscope, Fig. 10,I will focus on the ringed spherulite zone since we have more structural tags in this region. The spherulites appear to progressively deform into ellipsoidal forms elongated in the direction of drawing. However, little change in ring spacing occurs up to a draw ratio of three, Figure 11. The ring spacing does increase parallel to the draw direction (dotted line) relative to the ring spacing in the lateral direction (solid line). However, these changes are not sufficient to account for the extent of macroscopic deformation. Also, the changes in density and heat of melting are insignificant, indicating little change in structure.

Before examining the scanning electron micrographs of the deformed polyethylene, I would like to comment briefly on some of the characteristics of chromic acid etching. As indicated in Figure 12, the weight loss due to etching polyethylene is rather substantial. Surprisingly, our etching rate for polyethylene at 60°C is greater than the etching rate for polypropylene at 70°C reported by Armond and Atkinson (4). I would expect polypropylene would be etched at a faster rate due to the substantially greater number of pendant methyl groups.

We also discovered that the degree of etching doesn't appear to be consistent for the same etching times. The specimens shown in Figure 13 were all etched for 300 hours. However, the middle specimen in Figure 13 doesn't appear to be etched as much as its neighbors. Since the same six molar chromic acid solution was used in each case, but in different containers, we feel different amounts of oxygen from air were available to the specimens. Following this hypothesis, then the primary role of the chromic acid would be to catalyze the oxidative degradation of the polyethylene.

Disregarding these peculiarities of etching, the scanning electron micrographs do highlight the spherulite structure as intended. There are also a considerable number of cracks at spherulite boundaries in the slightly deformed specimen on the left -- the draw ratio of 1.0 is only an approximate value as this portion of the sample was also subjected to the same tensile load as the drawn material. Additional cracks are present at spherulite centers. These cracks may be due to deformation which the specimen has experienced coupled with the effects of etching. Specifically, we feel these cracks reflect crazed regions which have been accentuated by removal of material through etching since the crazes are more accessable to the etching solution. Thus, initial crazing occurs in relatively weaker regions where discontinuities in morphology exist.

At higher deformations -- micrographs b and c in Figure 13 -- the cracks appear to be orienting in the direction of the drawing (horizontal in Figure 13). The cracks at spherulite centers are more prevalent at these higher draw ratios. The considerably larger size and number of cracks at a draw ratio of 4.0 is probably a reflection of an increased number of crazes as well as more excessive etching.

The visual effect of progressive etching can be seen in Figure 14 in which micrographs for etching periods of 155, 310 and 900 hours are shown. Please note that the same specimens and magnifications have not been utilized. The etching process does appear to cause a progressive increase in the breadth and depth of the cracks. Some indication of the breadth and depth of a crack at the center of a spherulite can be gained from the higher magnification micrograph at the bottom-right in Figure 14. This crack or crator has a floor surrounded by the ringed spherulite pattern. The crack is also oriented in the direction of drawing (vertical).

CONCLUSIONS

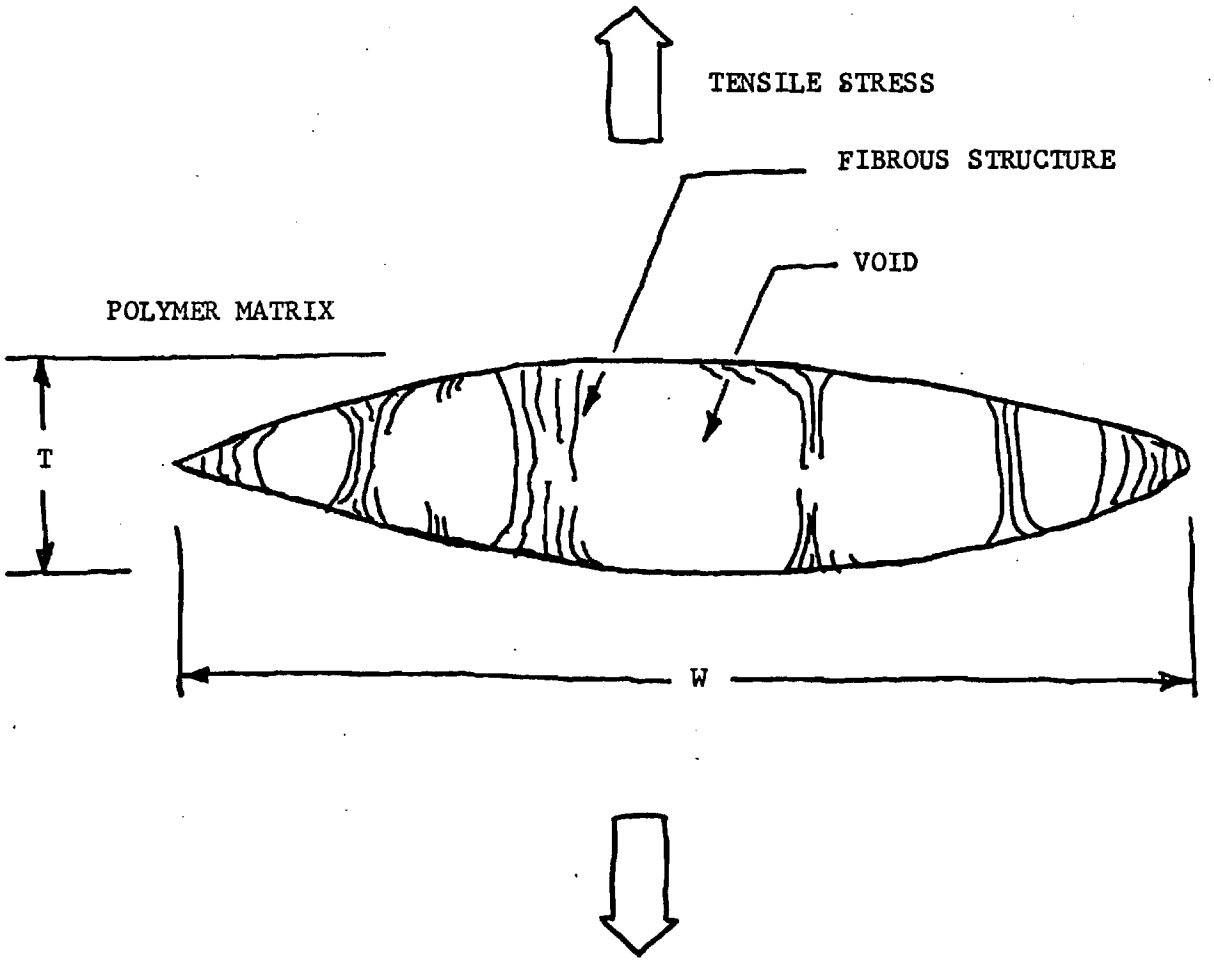
Our preliminary evidence indicates that mechanical failure by crazing is initiated at a very early stage of deformation in regions exhibiting morphological discontinuities. Spherulite centers and boundaries were common locations of large cracks in etched specimens, indicative of the existence of crazes in these regions before etching. With further deformation, the crazed regions and spherulites are elongated in the direction of drawing. However, the deformation of the ring pattern is considerably less than the macroscopic deformation, hence the deformation must be greater in the crazed regions. Little change occurs in the density or heat of melting up to a draw ratio of 4.0 which also indicates that the crystal structure has not been drastically altered. The formation of crazes in specific regions followed by elongation of these crazed regions form a microfibrous texture in the drawn material.

Our studies also indicate that the technique of cold sectioning followed by chromic acid etching is a useful method for preparing polyethylene samples for scanning electron microscope observations. We are presently refining our chromic acid etching technique to improve the quality of the SEM micrographs and to define the mechanism of etching.

REFERENCES

1. D. P. Thomas and R. S. Hagan, Poly. Eng. & Sci., 9, No. 3, 164 (1969).
2. J. D. Muzzy and D. Hansen, Text. Res. J., 41, 436 (1971).
3. A. Peterlin and K. Sakaoku, J. Appl. Phys., 38, 4152 (1967).
4. V. J. Armond and J. R. Atkinson, J. Materials Sci., 4, 509 (1969).

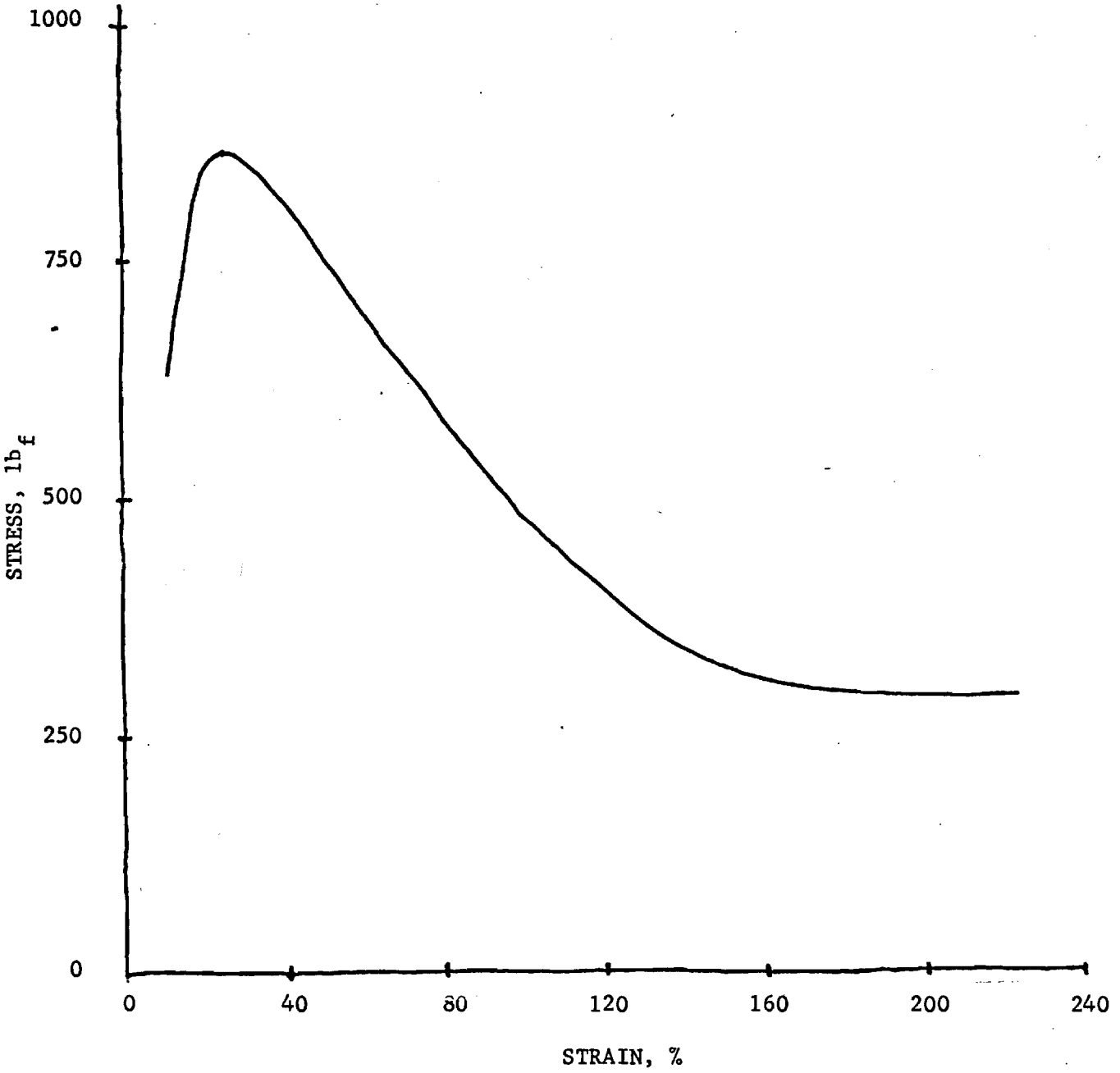
LIST OF FIGURES



Idealized model of a craze in a polymer. T is the thickness parallel to the imposed tensile stress and W is the width or diameter of the craze.

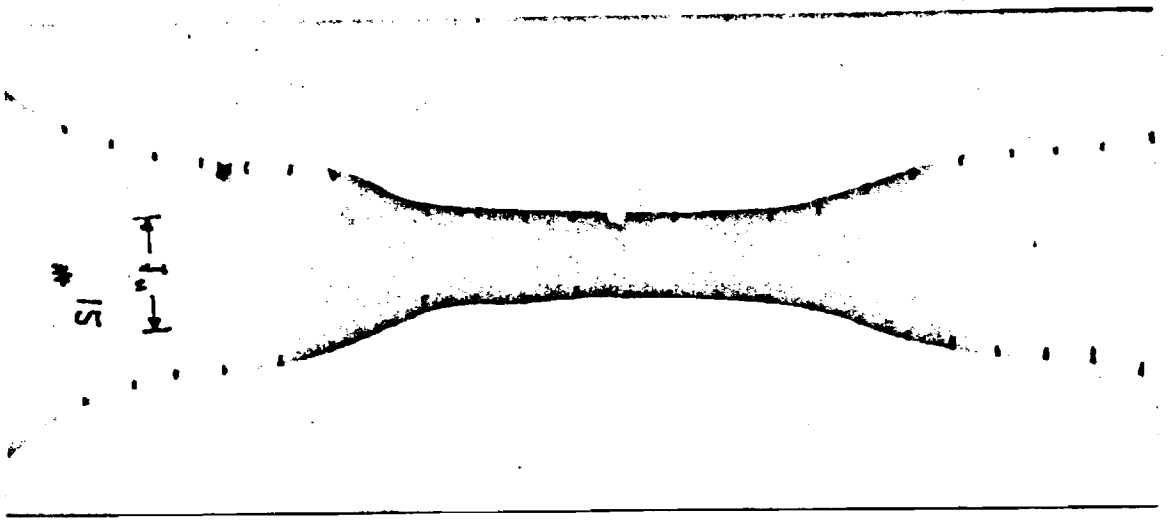
Figure 1.

Figure 2.



STRESS STRAIN CURVE OF SAMPLE NO. 12.

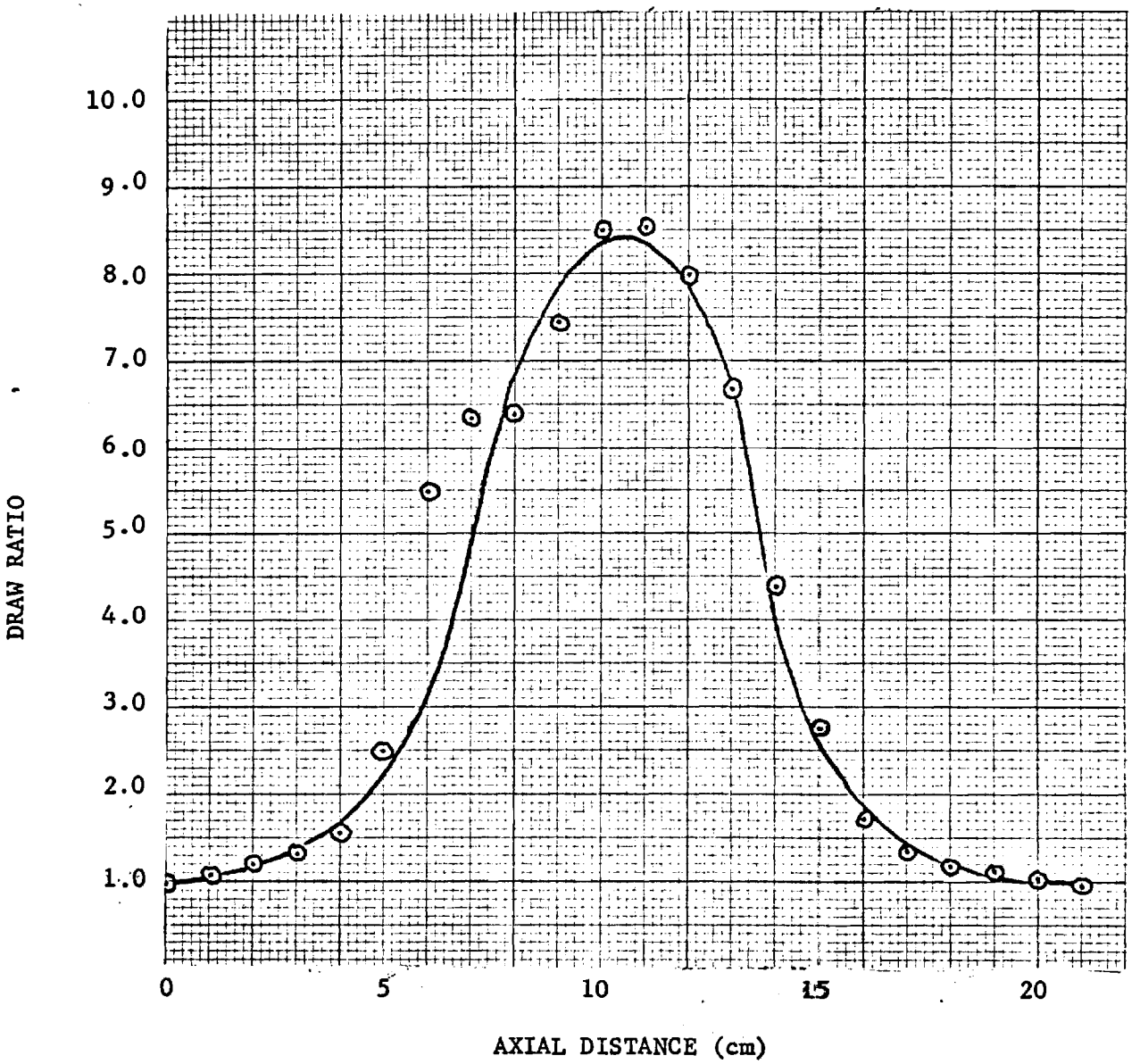
Initial Gauge Length of 2.50 inches.
Initial Gauge Cross-Sectional Dimensions of 0.22 inches x 2.00 inches.
Uniaxial draw rate of 40% per minute at 60°C.



Macrophotograph of Drawn High Density Polyethylene Sample.
Sample No. 12

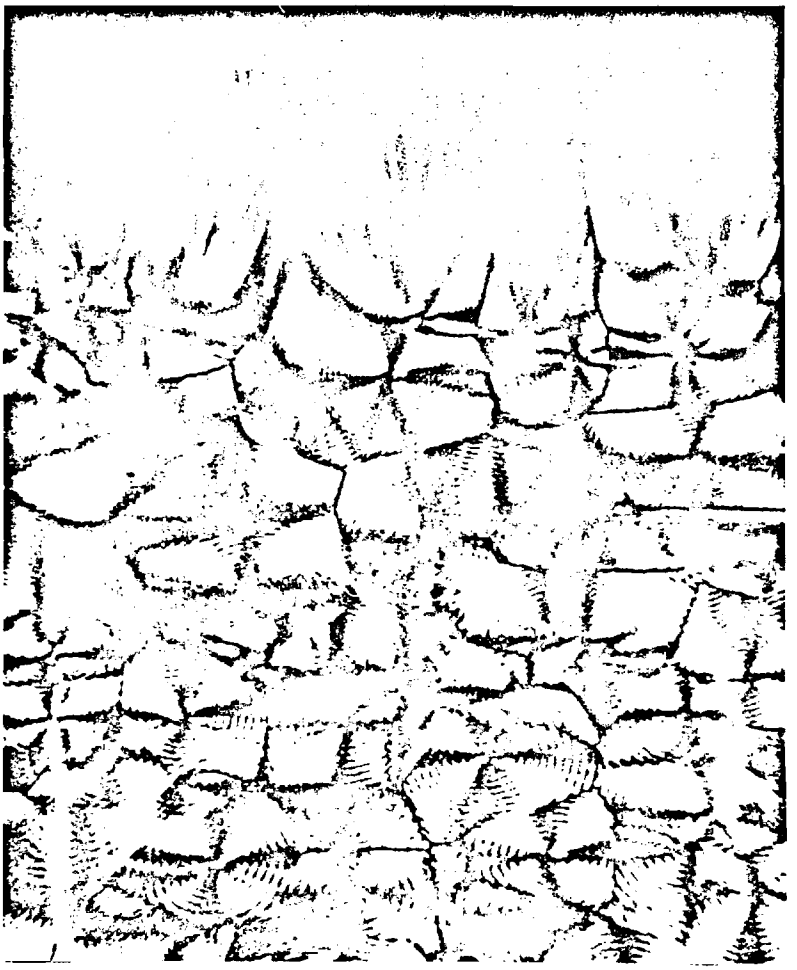
Figure 3.

Figure 4.



FINAL DRAW PROFILE
Sample #12

Initial Gauge Length of 2.50 inches.
Unaxial draw of one inch per minute
at 60°C.



Surface Structure
Sample #50
Undrawn Region
Crossed Nicols
440X

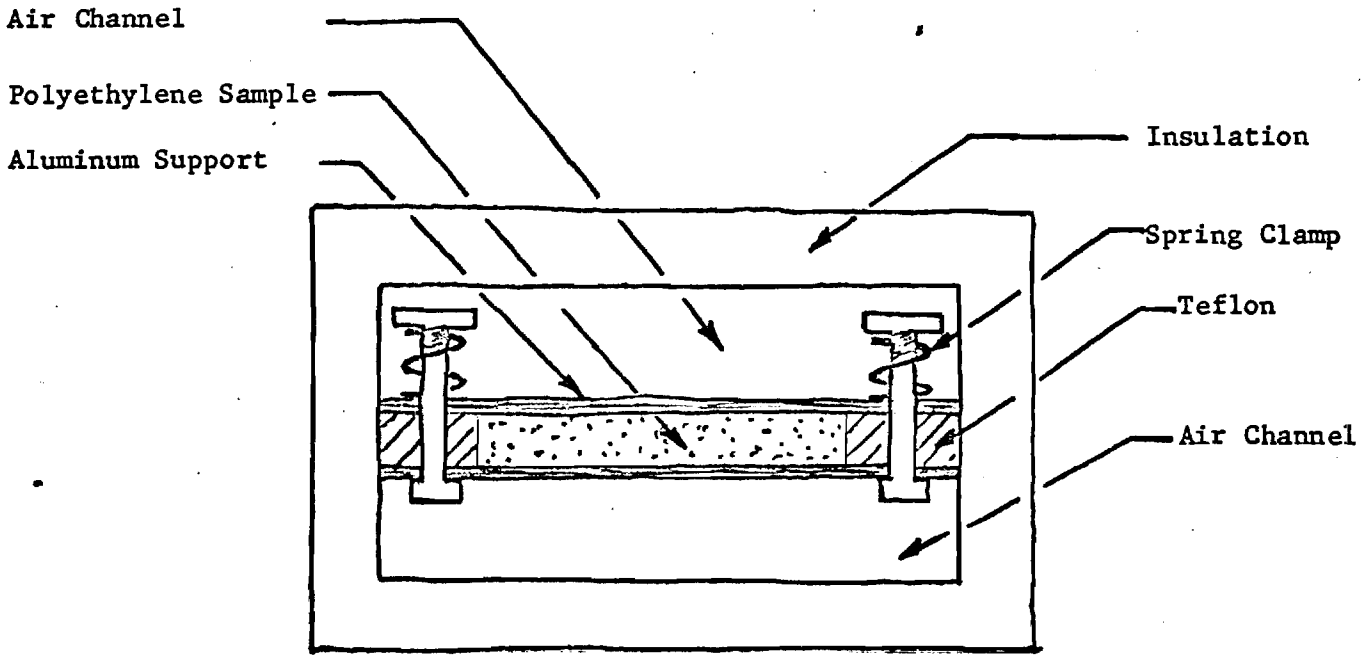
Figure 5.

Room Temperature Microtomed Surface
Sample No. 12
Scanning Electron Photomicrograph
270X

Figure 6.

Liquid Nitrogen Temperature Microtomed Surface
Sample No. 50
Scanning Electron Photomicrograph
410X

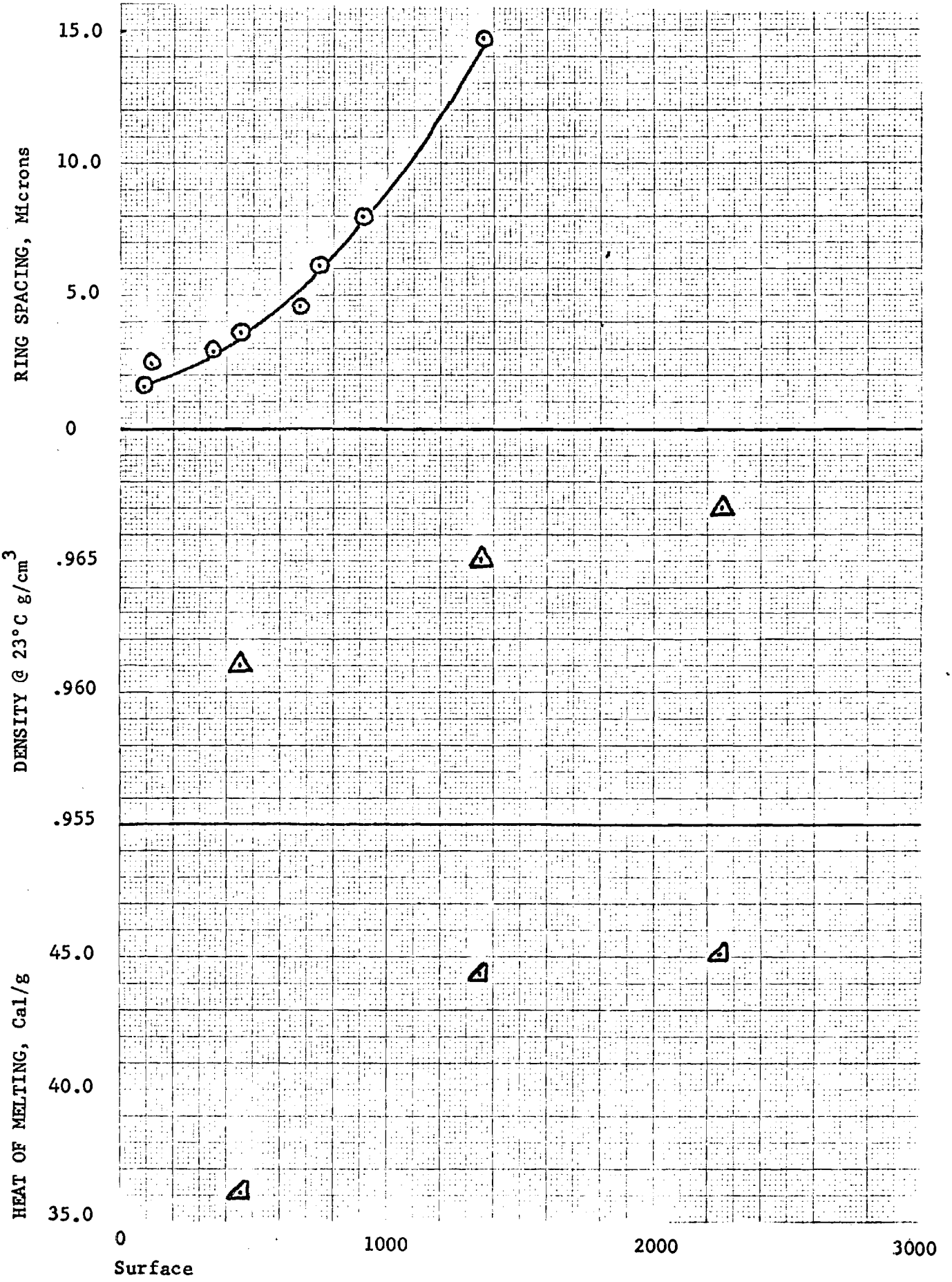
Figure 7.



THERMAL CRYSTALLIZER

Cross-sectional Schematic

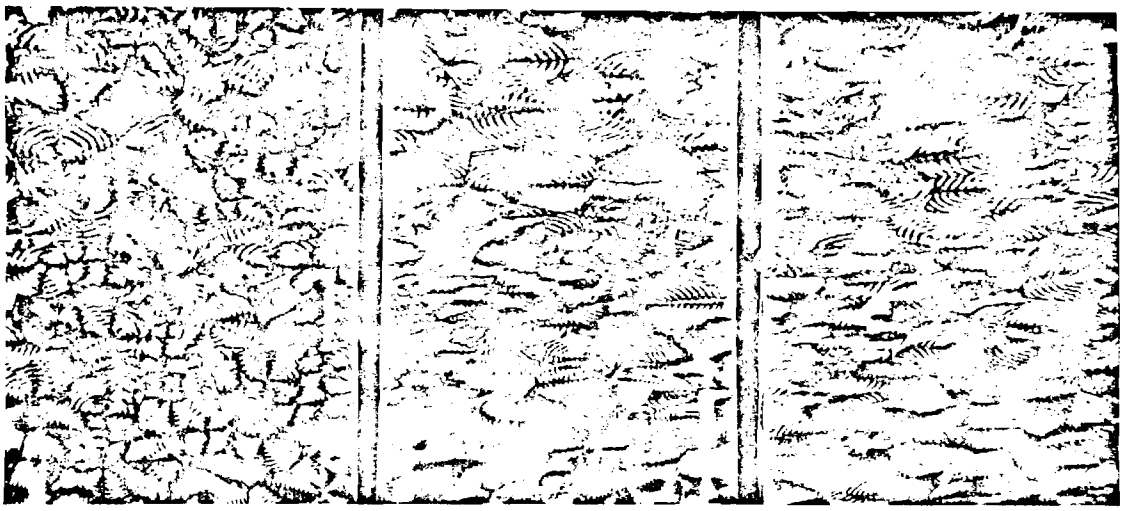
Figure 8.



STRUCTURE PROPERTIES VS POSITION IN BULK SAMPLE

Sample No. 50
Undrawn Region

UNIAXIAL DEFORMATION OF POLYETHYLENE SPHERULITES

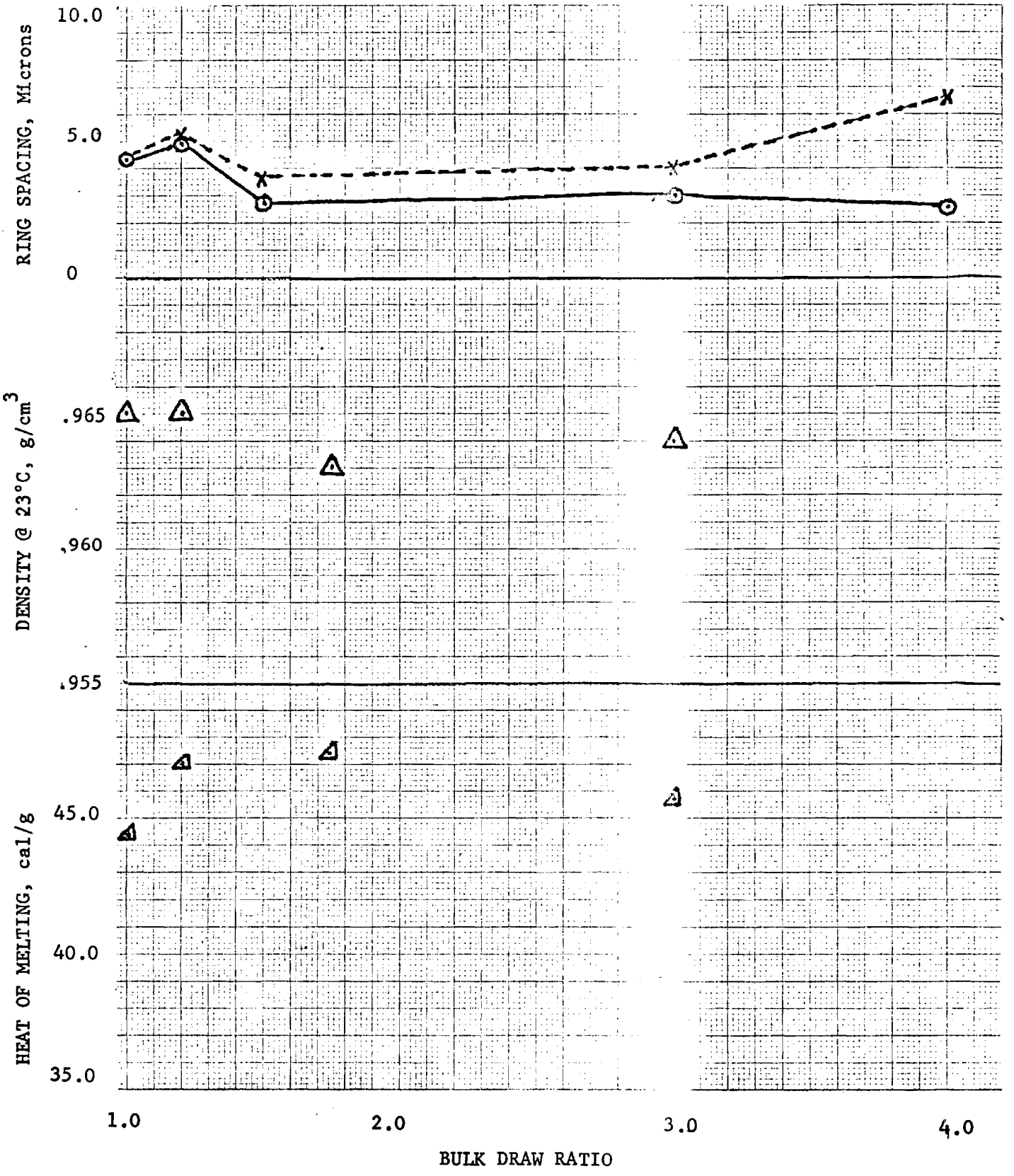


(a) (b) (c)

Crossed Nicols 200X, a) 1.0 Draw Ratio, b) 1.5 Draw Ratio
c) 3.0 Draw Ratio

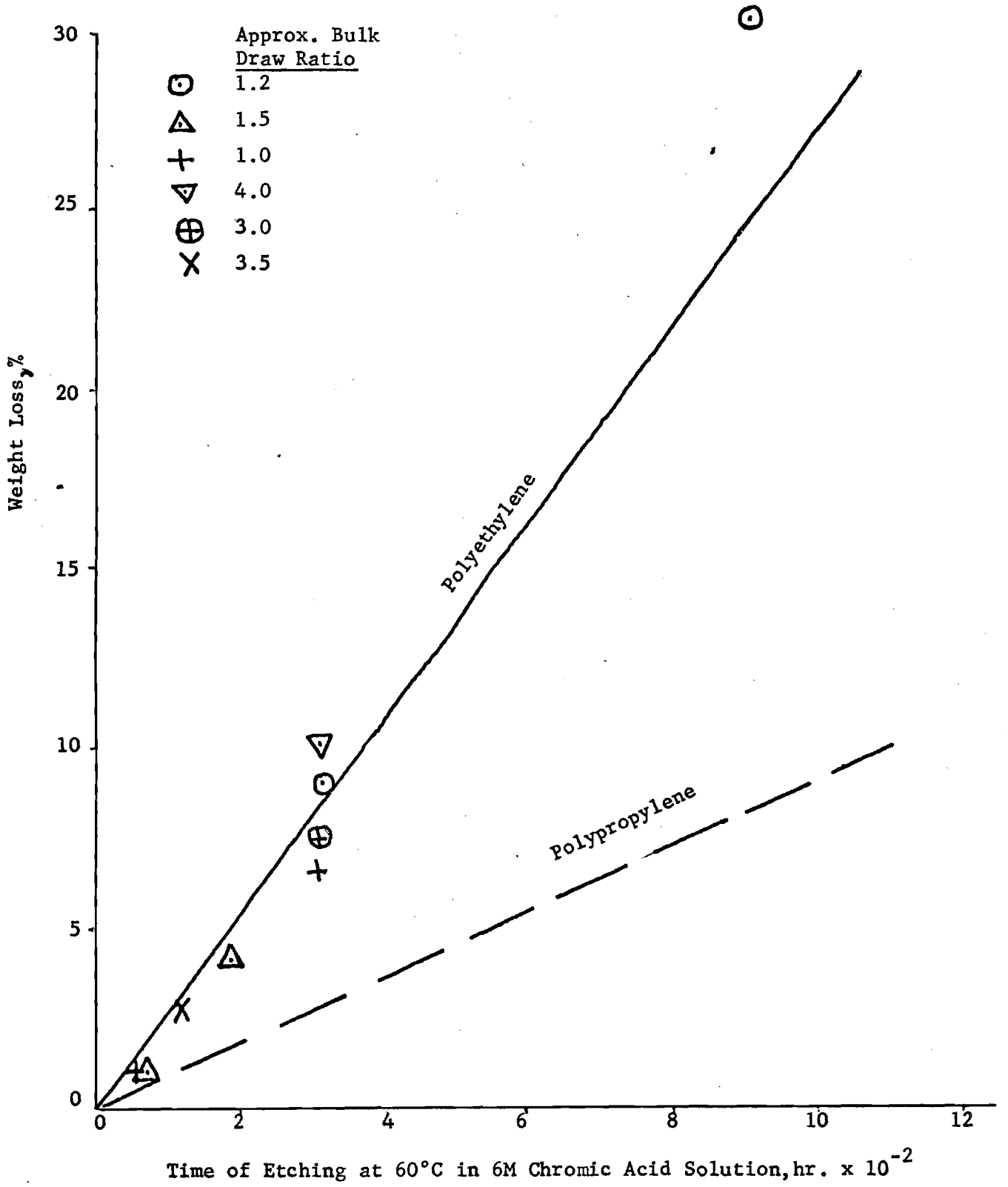
Figure 10.

Figure 11.



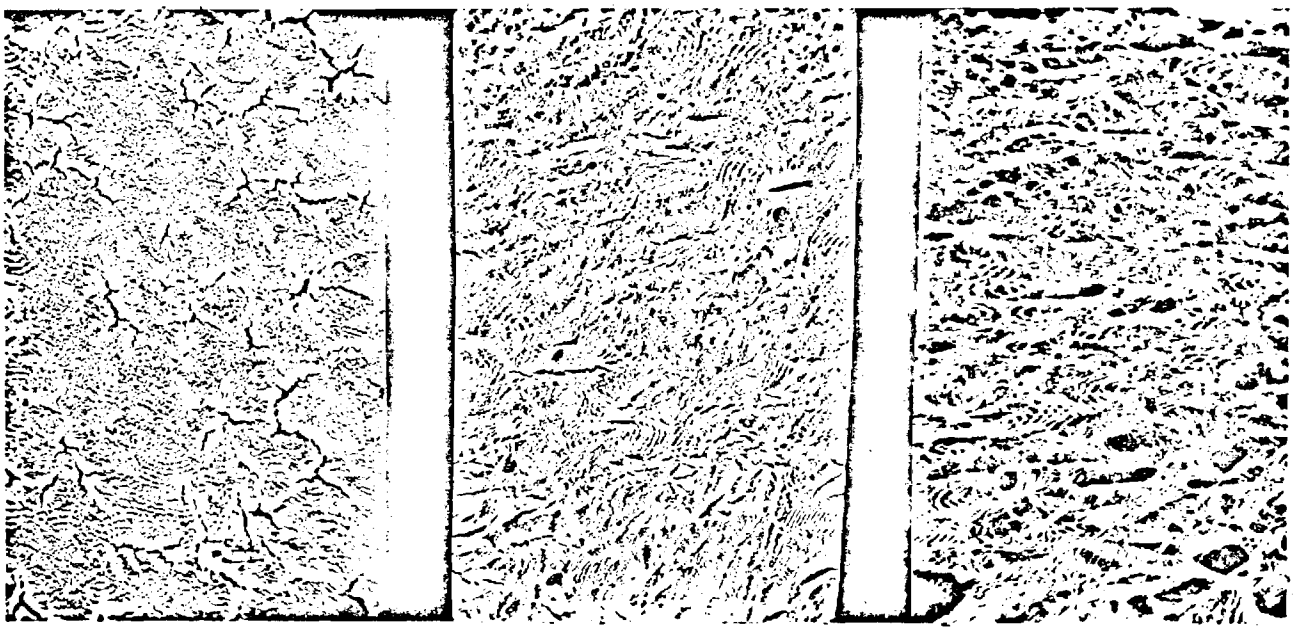
STRUCTURE PROPERTIES VS BULK DRAW

Measured at 400 microns below the surface
sample No. 50.



ETCHING OF HIGH DENSITY POLYETHYLENE

Figure 12.



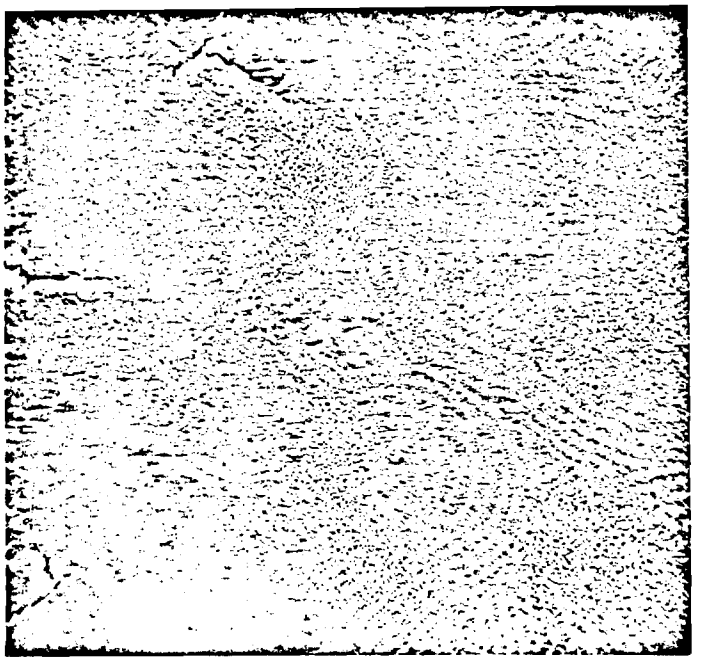
(a)
SEM 220 X
1.0 Draw Ratio

(b)
SEM 220 X
3.0 Draw Ratio

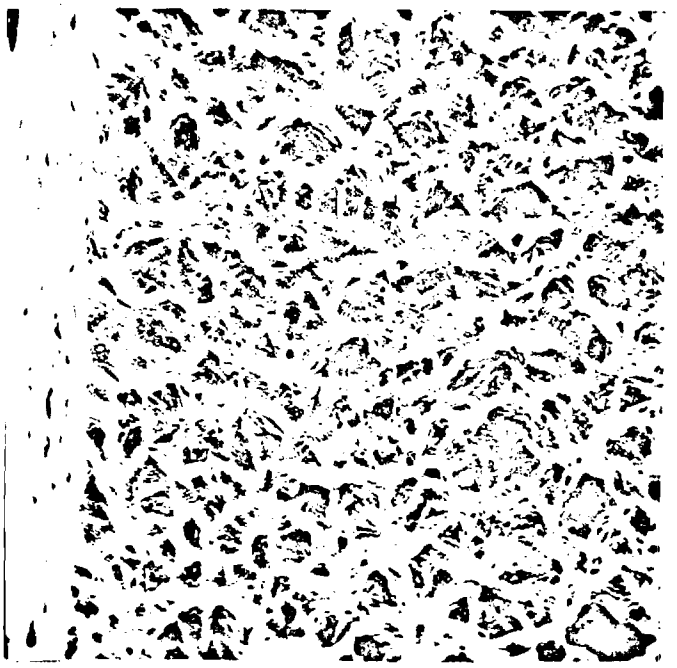
(c)
SEM 220 X
4.0 Draw Ratio

Figure 13.

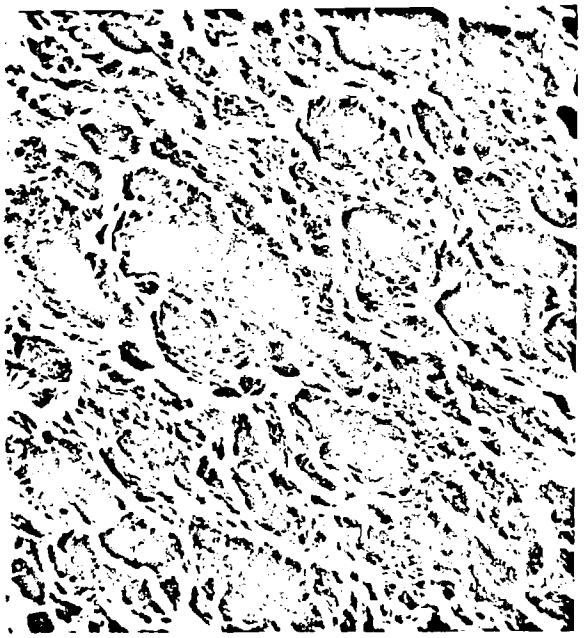
EFFECT OF PROGRESSIVE CHROMIC ACID ETCHING



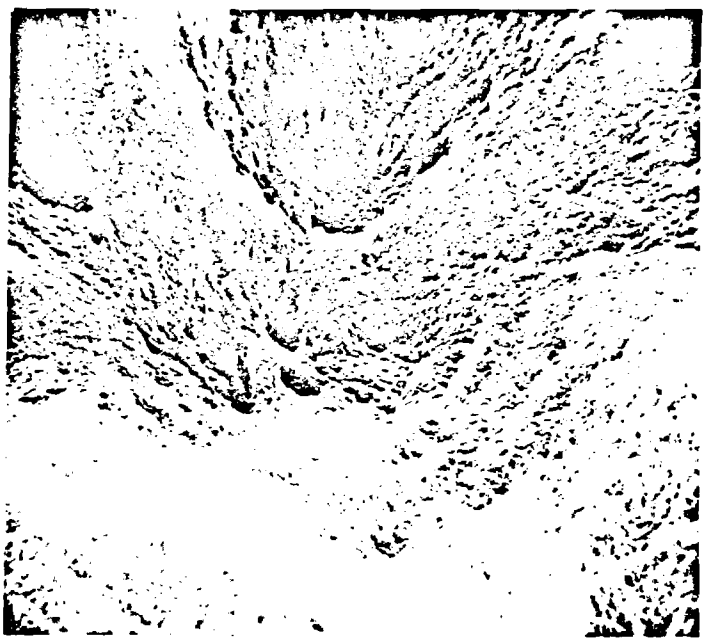
SEM of Polyethylene Sample Etched for 155 hr. in 6M Chromic Acid Solution at 60°C. Undrawn. 400X



SEM of Polyethylene Sample Etched for 310 hr. in 6M Chromic Acid Solution at 60°C. Uniaxial Draw of Approximately 25% in Vertical Direction. 220X



SEM of Polyethylene Sample Etched for 900 hr. in 6M Chromic Acid Solution at 60°C. Uniaxial Draw of Approximately 25% in Horizontal Direction. 220X



SEM of Polyethylene Sample Etched for 310 hr. in 6M Chromic Acid Solution at 60°C. Uniaxial Draw of Approximately 25% in Vertical Direction. 2400X

Figure 14.